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Research note

Growth of uniform nanoparticles of platinum by an economical approach at relatively low temperature

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KEYWORDS

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Abstract Current chemical methods of synthesis have shown limited success in the fabrication of nanomaterials, which involves environmentally malignant chemicals. Environmental friendly synthesis requires alternative solvents, and it is expected that the use of soft options of green approaches may overcome these obstacles. Water, which is regarded as a benign solvent, has been used in the present work for the preparation of platinum nanoparticles. The average particle diameter is in the range of $\sim 13 \pm 5$ nm and particles are largely agglomerated. The advantages of preparing nanoparticles with this method include ease, flexibility and cost effectiveness. The prospects of the process are bright, and the technique could be extended to prepare many other important metal and metal oxide nanostructures.

1. Introduction

New paradigms are shrinking our world. Innovations at the intersection of medicine, biotechnology, engineering, physical sciences and information technology are spurring new directions in commercialization and technology transfer [1].

Platinum (Pt) is an important catalyst used for the production of hydrogen by splitting water. It is also used for the reduction of many organic substrates. The selectivity and activity of platinum particles strongly depend on their sizes and shapes. It is believed that the chemical activities of platinum particles with different shapes are sensitive, not only to surface facets, but also to atomic structures [2].

Platinum nanoparticles with a high percentage of cubic, tetrahedral and octahedral like shapes have been synthesized by shape controlling techniques. Cubic based pyramid (half octahedron) platinum particles supported on NaCl have been reported in which the oriented substrate is the key for controlling the nucleation and growth morphology of particles. Cubic-like platinum particles with truncated corners have been grown by annealing in hydrogen gas at high temperature [3]. It has also been reported that controlling the shape and size of platinum particles is possible by changing the ratio of concentration of the capping polymer material to that of platinum cations, used in the reductive synthesis of colloidal particles in solution at room temperature [4]. Platinum nanoparticles in aqueous solution were synthesized by the novel electrochemical reduction of ionic platinum in the presence of polyvinylpyrrolidone (PVP), which is used as a protecting agent [5]. Using polyvinylpyrrolidone as a capping agent, snow-like platinum nanoparticles were synthesized by reducing H_2PtCl_6 with hydrogen [6]. Recently, a green synthetic approach has been developed for the reduction of platinum nanoparticles. The reduced nanoparticles gradually transform into nanowires, followed by evolution into cubic shapes of platinum nano cubes [7]. A range of other approaches has also been employed for the preparation of platinum nanoparticles [8–10].

However, the aforementioned routes involve environmentally malignant chemicals, which are toxic and not easily degraded in the environment. Environmental friendly synthesis requires alternative solvents, such as ionic liquids, liquid and water. Water is particularly attractive because it is inexpensive, environmentally benign and bestowed with many virtues, especially under supercritical conditions. It is, thus, of significance

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to design a facile and simple route to synthesize high-quality nanoparticles of Pt with a high yield.

In this work, we introduced an economical and environmentally benign approach to synthesize nanoparticles of platinum at $\sim$ 190 °C without expensive raw materials (e.g. Pt salts etc.), additives, organics and harmful gases. The short reaction time and relatively low reaction temperature are the distinct advantages of this method. Since only water has been used for the preparation of nanoparticles, we believe that the nanostructures so produced are bio-safe and biocompatible, and can be readily used for various applications. To the best of our knowledge, the synthesis of uniform nanoparticles of platinum without organics, catalyst and toxic solvents has not been reported so far in the literature.

2. Experimental

2.1. Materials and synthesis of nanoparticles

In a typical preparation process, 3 mg of platinum powder of micron size were added to 30 ml of de-ionized water in a glass vial. The reaction mixture was stirred, sonicated for about 10 min, transferred into a stainless steel Teflon lined metallic bomb of 50 ml capacity and sealed under inert conditions. The closed chamber was then placed inside a preheated box furnace, the mixture was heated slowly (2 °C/min) to 190 °C and maintained at this temperature for 6 h. The furnace was allowed to cool after the desired time and the resulting suspension was centrifuged to retrieve the product and washed several times with distilled water. The product was then finally air dried overnight.

2.2. Characterization of nanoparticles

The phase structure and purity of the prepared samples were characterized powder X-ray Diffraction (XRD) taken on a Philips XRD X'PERT PRO PW-3710 diffractometer, with 2θ ranging from 10–90°, using Cu Kα ($\lambda = 0.15141$ nm) radiation operated at 40 kV and 30 mA. The morphology of the products was carried out using a high resolution Scanning Electron Microscope (FEI, NNL 200), coupled with an energy dispersive X-ray spectrometer (EDX, GENESIS).

3. Results and discussion

The phase purity and crystal structure of the synthesized nanoparticles were investigated by X-ray diffraction measurement, as shown in Figure 1. The broad reflections of the synthesized sample indicate the nanocrystalline nature of the powder. All the broad diffraction peaks of the XRD pattern at $2\theta = 39.6, 47.4, 67.1, 81.2$ and $83.6°$, corresponding to the reflections (111), (200), (220), (311) and (222), respectively, which are consistent with the face centered cubic (fcc) structure of platinum, can be assigned to (JCPDS Card 04-0802), thus demonstrating the presence of crystalline Pt.

The morphology of the products was obtained by FESEM in which the solid sample was mounted on a conductive resin and the images of the products are shown in Figure 2. The low (Figure 2(a) and (b)) and high (Figure 2(c) and (d)) magnifications of nanoparticles of platinum, indicate that all products have almost identical morphology, except a few at the centre, which might be due to agglomeration. Water prepared

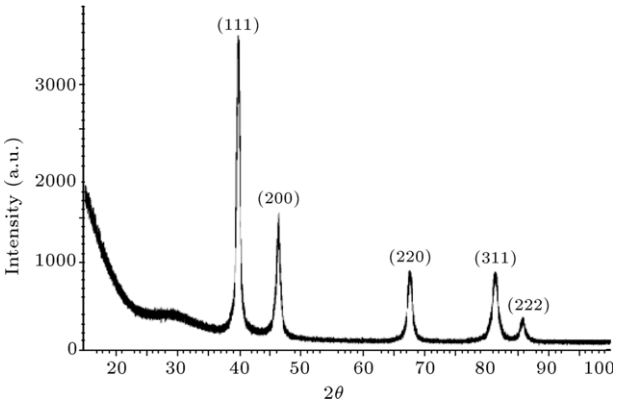

Figure 1: The XRD pattern of the Pt nanoparticles.

samples are prone to agglomeration. The images also confirm that the nanoparticles are grown at a very high density. The typical average diameters of the as-grown nanoparticles are $\sim 13 \pm 5$ nm. The particles are agglomerated as can be seem from micrographs.

The formation of platinum nanoparticles in the presence of water can be explained by simple chemical reactions. Initially, at 190 °C, and under pressure in a Teflon-lined stainless chamber, the Pt reacted with water and formed a protective platinum hydroxide ($Pt(OH)_2$) layer, with dissolved hydroxide ions, onto the surfaces of the platinum particles. The $Pt(OH)_2$ can be transformed into Pt crystals via the simple chemical reactions mentioned below

$$2Pt(OH)_2 \xrightarrow{\triangle} 2Pt + 2H_2O.$$

A similar study has been reported in cases of magnesium oxide by Shah and Quarshi [11]. From previous literature, the specially shaped materials are generally prepared in the presence of a template or other reducing agents [3]. The uniform sized particles, in our case, have been formed without any templates or surfactants. The simple explanation, at this time, is that water at elevated temperatures plays an essential role in the precursor material transformation, because the vapour pressure is much higher, and the state of water at elevated temperatures is different from that at room temperature. The solubility and reactivity of the reactants also change at high pressures and high temperatures, and high pressure is favorable for crystallization.

4. Conclusions

In summary, almost uniform nanoparticles of platinum, with diameters of 13 ± 5 nms, have been prepared via a simple reaction, without organics. In a more global way, the synthesis strategy used herein could be easily extended to other materials. Based on results, a possible formation mechanism was briefly discussed.

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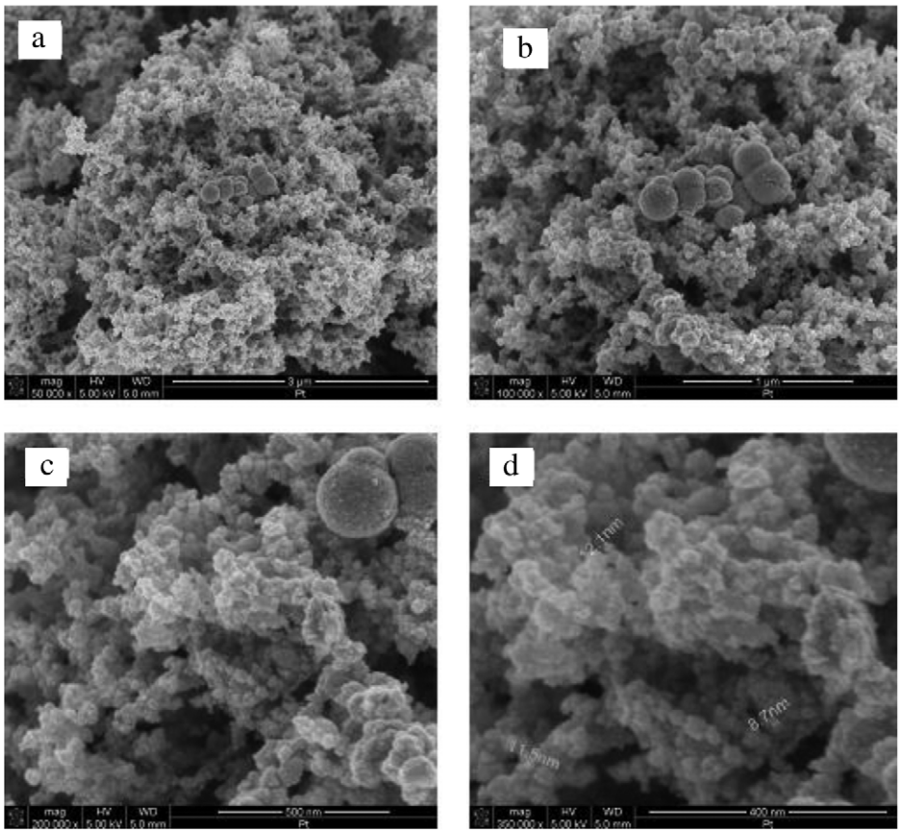

Figure 2: The FESEM images show the typical (a,b) low and high-resolution (c,d) images of Pt nanoparticles.

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